Tin(IV) Phosphonates with α-Layered Structure: Synthesis and Characterization

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The synthesis of layered compounds of the general formula $Sn(RPO_3)_2 \cdot xH_2O$ (R = phenyl, 2-carboxyethyl) and $Sn(ROPO_3)_2 \cdot xH_2O$ (R = dodecyl) are reported. These compounds are formed by the reaction of nitric solutions of $SnCl_4$ with the phosphonic acid or phosphoric ester followed by heating under reflux. The interlayer distances of 13.87, 15.37 and 32.70 Å for 2-carboxyethyl, phenyl and dodecyl derivatives, respectively, are determined by the XRD patterns. A linear relationship between the molar volume and the interlayer distance is observed suggesting an alpha structure similar to α-$Sn(HPO_4)_2 \cdot H_2O$. FTIR spectra show the formation of an Sn—O—P skeleton.

Keywords: *Layered structure; Tin(IV) phosphonate; Tin(IV) alkylphosphate*

Layered compounds formed by reaction involving tetravalent metals with phosphonic acids have received considerable attention, owing to their potential applications in catalysis and separation science.[1–6] Recent reports have shown that the catalytic and separation properties of these bidimensional systems arise because the intrinsic site disorder, which has been observed in functionalized silica and other solid supports, does not appear to occur.[5,7] This structural feature is important in chromatography or shape-selective catalysis.[8,9]

The preparation of these materials has been limited to some topochemical or exchange reactions of OH groups of layered compounds, such as zirconium phosphates.[5,10,11] In this case, the reaction is not complete because some available anion sites are not exchanged. Today, the availability of phosphonic acids and esters has opened the way to the preparation of new and interesting materials, with desired organic groups, by direct reaction with tetravalent metals.[7,12,13] However, in spite of their potential applications in cases where surface phenomena are important, the layered phosphonic (phosphate) derivatives containing post-transition tetravalent metals are incompletely studied.

In this work we show the preparation of new layered compounds of type $Sn(RPO_3)_x$ (R = phenyl, 2-carboxyethyl) and $Sn(ROPO_3)_x$ (R = dodecyl) by metathetical reaction from acidic solutions of $SnCl_4$ with the respective phosphonic acid and phosphoric ester. The solids obtained are characterized by chemical analyses (P, Sn), infrared (IR) spectroscopy, X-ray powder diffraction (XRD) and absolute density.

Experimental

Materials

Tin(IV) chloride (P.A. grade, Fluka) was purified by vacuum distillation. Phenylphosphonic acid (PPA) and 2-Carboxyethylphosphonic acid (CEPA), both from Aldrich, were used without further purification. Dodecyl phosphate (DPA) was prepared by the reaction of pyrophosphoric acid with dodecyl alcohol according to ref. 14.

Preparation

The following general procedure was used to prepare the samples: to a vigorously stirred solution of tin(IV) chloride (1 mol dm^{-3}) in nitric acid (3 mol dm^{-3}), was added a solution of the respective phosphonic acid or phosphate ester (1 mol

dm^{-3}) also in nitric acid (3 mol dm^{-3}). In the case of DPA a small amount of ethanol was used to increase the ester solubility. A molar ratio of P : Sn = 2.5 was used in all preparations. The white gel formed immediately after the addition of PPA or DPA solutions was redispersed with a few cm^3 of dilute nitric acid and treated under reflux for 24 h at 85–90 °C. For CEPA the gel was formed only *ca.* 2–3 h after heating the clear solution under reflux. The solid was separated by centrifugation, washed successively with deionized water until the pH of the washings was *ca.* 5 and the test for chloride ion proved negative, then dried in air. The yields were >80%.

Chemical Characterization

The samples were heated with a solid mixture of $NaOH : Na_2O$ (1 : 1) at 1000 °C. The resulting solid was disaggregated with warm water and dissolved in concentrated hydrochloric acid. Phosphorus was then determined spectrophotometrically as phosphomolybdate[15] and tin by flame atomic absorption.

Physical Measurements

The XRD patterns were recorded on a Shimadzu powder diffractometer, model XD-3A, using Cu-Kα, 1.5418 Å Ni-filtered radiation (30 kV and 20 mA) at a scan rate of 2° min^{-1}. The measurements were carried out with the sample spread on a conventional glass sample holder. IR spectra were recorded on a Nicolet 60SX-B FTIR spectrometer using Nujol and Fluorolube mull dispersion techniques. Measurements of absolute density were carried out on a Micromeritics Multivolume Pycnometer model 1305 using helium as the displacement gas.

Results and Discussion

Preparation, Composition and Crystallinity

Nitric solutions of $SnCl_4$ react instantaneously with PPA and DPA solutions forming a thick white gel. The presence of the ionogenic group CO_2H in CEPA could be responsible for the differences observed in the gel formation kinetics, as mentioned in the experimental section. However, for the analogous material obtained from the $ZrOCl_2$ solution and CEPA, gel formation follows the same pattern of behaviour as that observed for PPA and DPA with Sn^{IV}. The behaviour of the CEPA–Sn^{IV} system is similar to that of H_3PO_4–Sn^{IV}, where

the precipitation occurs only when the nitric oxide has been totally released.[16] We believe that the well known ability of $SnCl_4$ to form six-coordinated complexes with ligands containing $C=O$ groups,[17] prevents access of the PO_3H_2 group to the Sn^{4+} species in solution. Heating under reflux promotes the complex decomposition which creates the condition for P—O—Sn skeleton formation. Therefore, the gel formation for the system CEPA–Sn^{IV} can be controlled by the time of heat under reflux and temperature.

Table 1 lists the chemical compositions of the tin(IV) compounds prepared. It can be seen that the ratio P:Sn is very close to 2, and the compounds can be therefore formulated as $Sn(C_6H_5PO_3)_2 \cdot 1.7H_2O$, $Sn(C_3H_5O_2PO_3)_2 \cdot 2.4H_2O$ and $Sn(C_{12}H_{25}OPO_3)_2 \cdot 0.1H_2O$.

As noted previously for several analogous materials, the water molecules are located between the layers.[2] For these compounds it is clear that the amount of water is more closely related to the hydrophobic character rather than to the length of the organic chain. Fig. 1 displays the XRD patterns for PPA, CEPA and DPA tin(IV) compounds.

The poor definition of the peaks, mainly at $2\theta > 10°$, may be attributed to an incipient stage of crystallization. In order to obtain materials with a higher degree of crystallization, variations in time and concentration of the phosphonic acid and phosphoric ester were attempted. For the layered compounds $Zr(HPO_4)_2 \cdot H_2O$ and $Zr(HPO_3)_2 \cdot nH_2O$, these procedures have allowed us to obtain samples with a high degree of crystallinity.[2,5,19] However, for the compounds described in this paper, results were unsuccessful, i.e. the solubilization–reprecipitation mechanism, responsible for the increase of crystallinity observed for similar zirconium compounds,[19,20] was not operative. This behaviour is probably due to the low solubility of tin(IV) compounds in the reaction medium.

Structural Model and Interlayer Distances

The main features of the XRD patterns (Fig. 1) are the presence of well defined peaks in the region of $2\theta < 10°$. If we consider similar, better known layered phosphonates involving tetravalent metals other than Sn, the first reflection is straightforwardly assigned to the 002 family of planes, which is related

Table 1 Chemical composition of tin(IV) derivatives of phosphonic acids and phosphate ester

R	P:Sn	H_2O/mol^a
phenyl	2.10	1.7
2-carboxyethyl	1.90	2.4
dodecyl	1.95	0.1

[a] Estimated from TG measurements.[18]
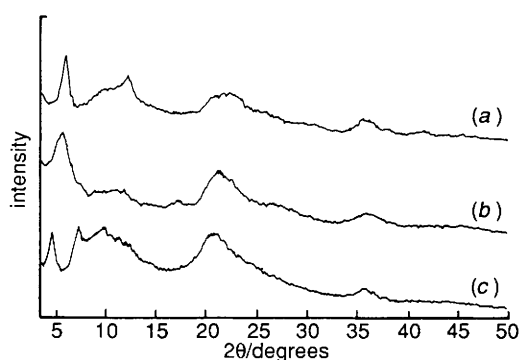
Fig. 1 XRD patterns for tin(IV) layered compounds: (a) $Sn(C_3H_5O_2PO_3)_2$; (b) $Sn(C_6H_5PO_3)_2$ and (c) $Sn(C_{12}H_{25}OPO_3)_2$

Table 2 Density and calculated and observed interlayer distance for $Sn(RPO_3)_2$ and $Sn(ROPO_3)_2$ compounds

R	density/ g cm^{-3}	d(002) calculated/ Å	d(002) observed/ Å	$\Delta(\%)^a$
hydroxyl	3.12^b	—	7.80^b	—
2-carboxyethyl	2.20^c	13.10	13.87^c	5.9
phenyl	1.92^c	14.70	15.37^c	4.6
dodecyl	1.32^c	32.70	33.54^c	2.7

^{a} $\Delta(\%) = (d_{obs} - d_{calc})/d_{obs} \times 100$; ^{b} from ref. 21; ^{c} this work.

to the separation of layers. Table 2 shows the interlayer distances for tin(IV) phosphonates and phosphates and for $Sn(HOPO_3)_2 \cdot H_2O$, i.e. α-SnP, which are included for comparison.

The interlayer distances shown in Table 2 are in agreement with those reported for the analogous zirconium and titanium compounds,[7,12,13] and reveal a dependence on the length of the organic group. Fig. 2 shows a plot of interlayer distance versus molar volume (molecular weight over density) for the tin(IV) compounds. The straight line which fits the points has a slope of 0.0665, very close to 0.0683 obtained for similar well established layered compounds.[12] This result can be explained in terms of the ideas of Alberti et al.,[12] who argued that in the case of zirconium(IV) phosphonate derivatives, the structures of the compounds are similar to that of $Zr(HPO_4)_2$, that is the OH of the phosphate group is replaced by R or O—R groups. For the tin(IV) compounds studied here this assumption can also be applied. By analogy we would have the same type of layered structures i.e., an α-type structure as represented in Fig. 3 for a dodecyl phosphate compound.

Table 2 shows estimated interlayer distances for the tin(IV) phosphonates (phosphate), considering the length of the organic groups using the Körney–Szirtes model,[22] adapted for tin(IV) compounds. Although the deviation (Δ) can be accepted it is important to note that the estimated value does not take into account the possible orientations of the pendant group with respect to the plane of the tin(IV) atoms. Furthermore, the samples are not well crystallized, so that the value of the (00l) reflections can exhibit variations. For example, in the case of $Zr(HPO_3)_2$ values from 5.99 to 5.57 Å are observed on going from a semicrystalline to a crystalline phase.[19] The
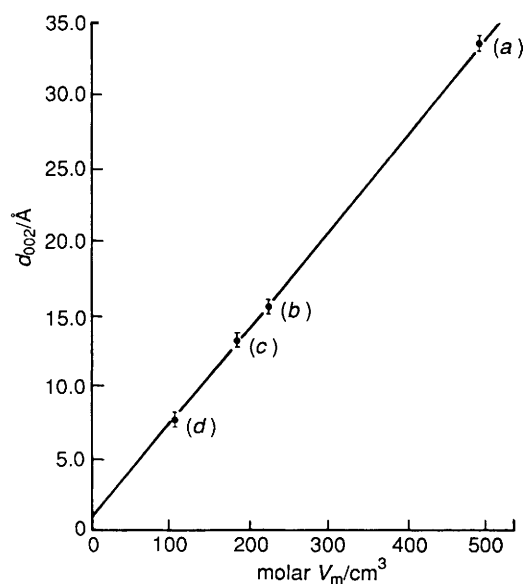

Fig. 2 Relationship between the interlayer distance and the molar volume for tin(IV) layered compounds (see Table 2)
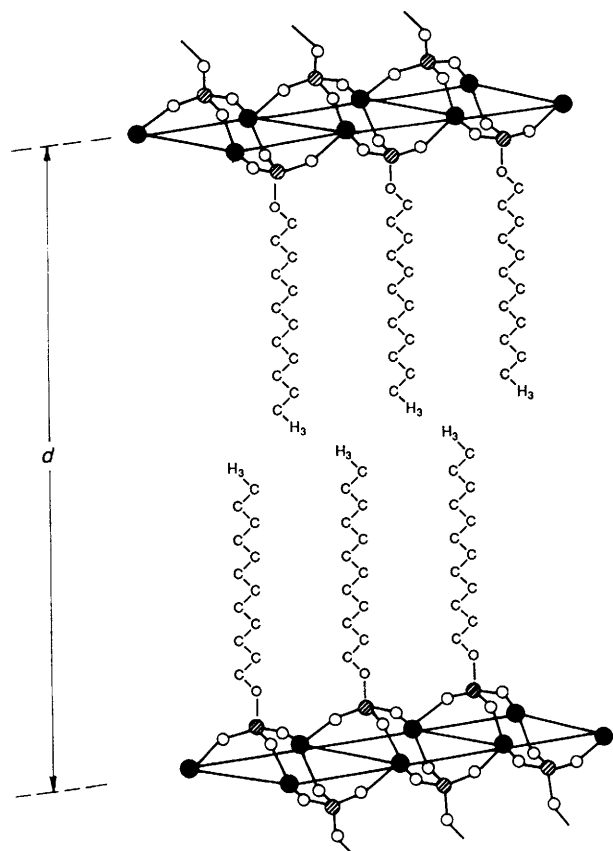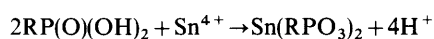
Fig. 3 Schematic representation of the α-structure for $Sn(C_{12}H_{25}OPO_3)_2$ (adapted from ref. 2; d = interlayer distance)

Fig. 4 IR spectra (4000–1400 cm^{-1}) for tin(IV) layered compounds: (a) Sn $(C_3H_5O_2PO_3)_2$; (b) $Sn(C_6H_5PO_3)_2$ and (c) $Sn(C_{12}H_{25}OPO_3)_2$; n = nujol bands
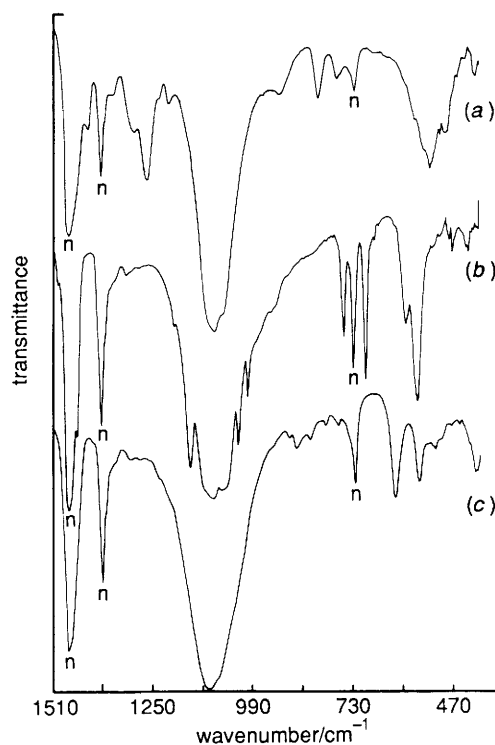
Fig. 5 IR spectra (1510–340 cm^{-1}) for tin(IV) layered compounds: (a) $Sn(C_3H_5O_2PO_3)_2$; (b) $Sn(C_6H_5PO_3)_2$ and (c) $Sn(C_{12}H_{25}OPO_3)_2$ n = nujol bands

same behaviour was observed for $Zr(HO_2CCH_2CH_2PO_3)_2$, obtained both in the presence and absence of hydrofluoric acid as a crystallization promoter.[7] In both cases values of interlayer distances for the poorly crystallized samples are larger than for the well crystallized ones.

Infrared Spectra

The IR spectra in the region of 4000–1400 cm^{-1} and 1400–300 cm^{-1} are shown in Fig. 4 and 5. The first observation is that the broad bands in the region of 3700–2250 cm^{-1}, due to the stretching and bending modes of the P—OH groups in the free acid[23] are absent in the spectra of the tin(IV) derivatives. The second observation of note is the presence of bands near 3386, 3420 and 3520 cm^{-1}, attributable to OH stretching modes, as well as bands at 1638, 1637 and 1632 cm^{-1}, due to the bending OH_2 modes of water for the PPA, CEPA and DPA derivatives, respectively. The relative intensities of these bands confirm the data shown in Table 1 with respect to water content.

In comparison with the free acids, the region 1250–900 cm^{-1}, where the P=O and P—O(H) stretching modes[23] are expected, shows marked modifications. For all samples broad bands centred at 1088, 1079 and 1101 cm^{-1} for phenyl, 2-carboxyethyl and dodecyl groups, respectively, are observed. These findings show clearly that formation of the R—P—O—Sn skeleton occurs in the system and reflect the formation of the PO_3 group by transformation of P=O to P—O and ionization of PO—H bonds as follows:
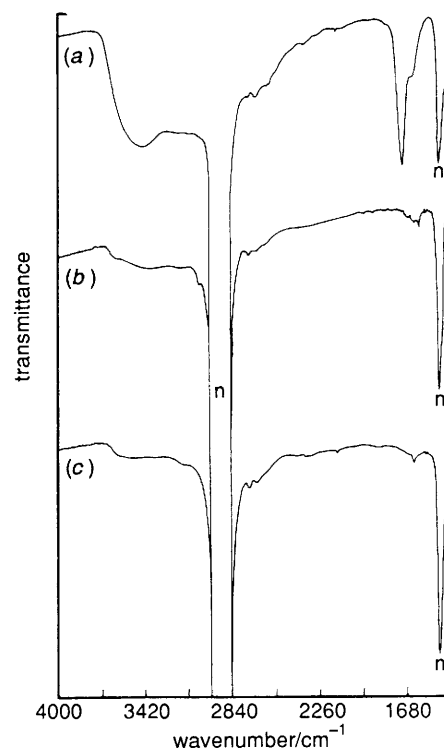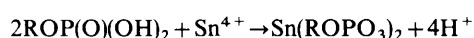
$$2RP(O)(OH)_2 + Sn^{4+} \rightarrow Sn(RPO_3)_2 + 4H^+$$

or

$$2ROP(O)(OH)_2 + Sn^{4+} \rightarrow Sn(ROPO_3)_2 + 4H^+$$

Similar features in the IR spectra in the region of P—O absorptions have been observed for other layered compounds involving tetravalent metals and phosphorous acid (H_3PO_3), and can be attributed to the same effect.[19] Furthermore, the band assigned to the C=O stretching at 1695 cm^{-1} in the

free 2-carboxyethylphosphonic acid[23] is little perturbed, indicating that the chemical nature of the carboxy group is preserved upon formation of the layered structure.

Conclusions

Layered compounds of type $Sn(RPO_3)_2$ and $Sn(ROPO_3)_2$ can be readily prepared by the reaction of nitric solutions of $SnCl_4$ with the respective phosphonic acid or phosphoric ester. The formation of these compounds depends on the nature of the organic group R being more rapid for PPA and DPA than for CEPA. A linear dependence of the molar volume *versus* the interlayer distance is observed and hence an α structure is proposed for the tin(IV) derivatives, analogous with similar zirconium(IV) compounds.

Preliminary results from the ^{119}Sn Mössbauer spectra of $Sn(C_{12}H_{25}OPO_3)_2$ show that an order–disorder transition occurs at low temperatures.[24] An in-depth study of this transition and the thermal behaviour of this family of compounds is in progress in our laboratory.

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